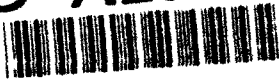


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## **A Review of the Calcium Thionyl Chloride Electrochemical System**

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Electronics Technology and Devices Laboratory

**April 1991**

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Citing work from the open literature and from Government-sponsored contractual efforts, research on the calcium thionyl chloride electrochemical system is reviewed. Progress has been made toward enhancing the performance at 25 deg C by adding sulfur dioxide to the electrolyte, and by using cathodes comprised of a blend of high- and low-surface area carbons. Sulfur dioxide raised electrolyte conductivity and improved low-temperature (-30 deg C) performance; still, low-temperature capacity remains poor. With strontium tetrachloroaluminate salt in the electrolyte, the film that formed on calcium was altered, which reduced rapid corrosion of calcium effectively, especially when used in conjunction with sulfur dioxide. With careful engineering, this may be a viable system for special applications.

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## INTRODUCTION

One of the primary goals in the development of new battery chemistries is the safe use of high-energy systems. The lithium thionyl chloride cell chemistry exhibits high energy density and high rate capability over a wide range of temperatures ( $-30^{\circ}$  to  $55^{\circ}\text{C}$ ). However, abuse conditions may lead to fire or explosion in lithium thionyl chloride batteries. When driven into reversal, lithium metal plates at the cathode and can create an internal short circuit. The heat generated from shorting may melt lithium (mp  $180^{\circ}\text{C}$ ) and cause internal cell pressure to increase, with serious consequences. The more benign event is a "controlled" cell venting; the more serious is a sudden cell explosion due to thermal runaway that is caused by reaction of molten lithium with sulfur (one of the discharge products of  $\text{SOCl}_2$  reduction).

Because it addresses these safety concerns, the calcium thionyl chloride chemistry has attracted attention since the late 1970's. Initially, there was hope that this chemistry could be equal in energy to lithium primary chemistries, yet far safer, because the melting point of calcium is  $839^{\circ}\text{C}$ . Plating of calcium in thionyl chloride is extremely difficult, and safety studies have shown calcium cells to be resistant to abuse. The goal was to develop an ultra-safe cell that would be so resistant to abuse that a ventless cell design could be employed.

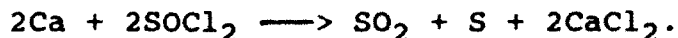
Although considered safe, several performance problems were readily observed with  $\text{Ca/SOCl}_2$  cells. Open-circuit potentials, although theoretically close to that of the  $\text{Li/SOCl}_2$  couple (3.65 V), were several tenths of a volt lower. Capacities at ambient temperature were poor, underutilizing the cathode capacity established in lithium systems. Performance at  $-30^{\circ}\text{C}$  (a requirement in military specifications) under moderate loads ( $5 \text{ mA cm}^{-2}$ ) did not exist. Finally, there was a high rate of anode corrosion, which precluded cell storage.

One challenge facing investigators was to make a more conductive electrolyte that would improve low-temperature performance and prevent corrosion of the calcium. Anode activation and performance at low temperatures were also major concerns. The improvement of cathode capacities was less troubling, but equally pursued. Most important, design improvements were not to compromise the inherent safety features of  $\text{Ca/SOCl}_2$ .

This paper summarizes studies of the electrolyte, cathode, anode, and anode corrosion of Ca/SOCl<sub>2</sub> cells. Some performance and safety testing of laboratory cells and full hardware cells are also given; but due to the differing test vehicles and loads applied during discharge, comparisons between investigators are difficult.

## GENERAL CHEMISTRY

Typically, the Ca/SOCl<sub>2</sub> cell consists of a calcium anode, carbon cathode current collector, and a thionyl chloride electrolyte composed of a tetrachloroaluminate salt (AlCl<sub>4</sub><sup>-</sup>) with Ca<sup>2+</sup> or Sr<sup>2+</sup> as the counterion. Upon discharge, the reaction of calcium with thionyl chloride is similar to that of lithium:



Because CaCl<sub>2</sub> is insoluble in a SOCl<sub>2</sub> electrolyte, ambient temperature cell failure is due to the passivation of the cathode with electrically insulating CaCl<sub>2</sub>. Unlike LiCl, which forms a crystalline deposit, CaCl<sub>2</sub> is glassy, amorphous, and evidently more efficient at passivating the cathode.<sup>1</sup> Thermodynamically, this reaction should consume the reactants spontaneously, but CaCl<sub>2</sub> forms a passivating layer on the calcium anode that protects it from rapid corrosion.

Although the theoretical potential of the Ca/SOCl<sub>2</sub> couple should be between 3.6 and 3.7 V, observed values are about 3.0 to 3.2 V at room temperature. In an interesting attempt to turn this discrepancy into an advantage, calcium was considered for use in implantable medical devices that require warning of end of life.<sup>2</sup> Because lithium cells have a flat voltage profile until very near their end of life, a composite anode was fabricated with a calcium inner core. When the lithium was exhausted, the (lower) potential of calcium foreshadowed end of life before the remaining cell capacity became dangerously low. Unfortunately, it was found that the higher the calcium content, the higher the corrosion.

## ELECTROLYTE STUDIES

An obvious starting place for improvement was the electrolyte, since Ca(AlCl<sub>4</sub>)<sub>2</sub>-SOCl<sub>2</sub> is only 30 percent as conductive<sup>3</sup> as LiAlCl<sub>4</sub>-SOCl<sub>2</sub>. An approximately 1 M solution has a conductivity<sup>3-8</sup> on the order of  $6 \times 10^{-3} \text{ S cm}^{-1}$ , and 1.9 M electrolyte<sup>7</sup>  $4.1 \times 10^{-3} \text{ S cm}^{-1}$ .

Based upon conductivity data, it was determined that the optimal concentration of  $\text{Ca}(\text{AlCl}_4)_2\text{-SOCl}_2$  for low-temperature discharge is approximately 0.7 M, and for 10-60°C, it is about 1.25 M.<sup>7,9</sup>

The density of 2 M  $\text{Ca}(\text{AlCl}_4)_2\text{-SOCl}_2$  solution at temperatures from -20° to 60°C ranges from about 1.89 to 1.78 g cc<sup>-1</sup>, and from 1.75 to 1.61 g cc<sup>-1</sup> for a 0.4 M solution.<sup>7</sup> A 1.9 M solution is very viscous, even at room temperature. A 1.2 M solution shows a sharp increase in viscosity below 0°C; whereas a concentration of 0.95 M shows gradual increase in viscosity with decreasing temperature.<sup>7</sup> As temperatures were decreased, no salt precipitation was noticed down to -30°C for a 1.9 M solution,<sup>9</sup> and -40°C for 1.8 M solution.<sup>10</sup> At -50°C, solutions from 1.0 to 1.8 M froze, but no salt appeared to precipitate out.<sup>10</sup> An explanation for no salting out is based on studies<sup>11</sup> of  $\text{LiAlCl}_4\text{-SOCl}_2$ , where it was proposed that the system behaves as a mixture of two miscible liquids,  $\text{SOCl}_2$  and  $\text{LiAlCl}_4 \cdot 2\text{SOCl}_2$ , rather than a salt solution. It was supposed that  $\text{Ca}(\text{AlCl}_4)_2\text{-SOCl}_2$  behaves in a similar manner.

Numerous salts and cosolvents were tried in order to improve on the performance of  $\text{Ca}(\text{AlCl}_4)_2$ . Although  $\text{LiAlCl}_4$  forms a conductive electrolyte, lithium is able to plate out, and therefore might cause the same hazards under abuse conditions as an all-lithium cell. Further,  $\text{Ca/SOCl}_2$  cells with  $\text{LiAlCl}_4$  salt showed excessive corrosion<sup>12</sup> during storage and during discharge at temperatures greater than 100°C. The OCV of a calcium cell stored at 200°C was zero in less than 10 days ( $\text{Ca} \rightarrow \text{CaCl}_2$ ), whereas no changes were observed in a lithium cell after 30 days.<sup>12</sup>

It was found that additions of  $\text{SO}_2$  to  $\text{Ca}(\text{AlCl}_4)_2$  electrolyte increased conductivity 40 to 50 percent over temperatures<sup>8,13</sup> ranging from -40°C to 50°C. Saturating a 1.2 M solution with  $\text{SO}_2$  (approximately 7% V/V) increased specific conductivity at room temperature<sup>4-6</sup> from 0.006 to 0.009 S cm<sup>-1</sup>. The addition of 7 to 12 percent  $\text{SO}_2$  reduced anode polarization at low temperatures and improved cathode capacity and load voltage at room temperature.<sup>4-6,10,14,15</sup> Raman spectroscopy<sup>16,17</sup> in  $\text{SOCl}_2$ , as well as Raman<sup>18</sup> and NMR<sup>19</sup> studies in sulfonyl chloride ( $\text{SO}_2\text{Cl}_2$ ) showed that the predominant interaction of  $\text{SO}_2$  is with  $\text{Ca}^{2+}$  ions. Solvation of these cations is believed to account for better cell performance by decreasing viscosity, increasing cation mobility, and, possibly, by altering the morphology of the  $\text{CaCl}_2$  deposited in the cathode. A 0.9 M  $\text{Ca}(\text{AlCl}_4)_2\text{-SOCl}_2$  electrolyte with either 7, 11, or 20 percent  $\text{SO}_2$  was evaluated in order to determine optimum sulfur dioxide concentration.<sup>20</sup> The 20 percent (V/V)

concentration offered the best performance (actually making a 0.72 solution). More recently, Peled et al. reported that a  $\text{Sr}(\text{AlCl}_4)_2$  electrolyte containing a combination of 20 percent  $\text{SO}_2$  and 0.3 percent of an undisclosed additive enhanced rate capability and reduced corrosion to four percent per month<sup>21</sup> at 70°C. Without these additions, corrosion was 11 to 12 percent. Improved low-temperature performance was also achieved by adding 10 percent bromine to the electrolyte.<sup>22</sup>

Extensive work with many other cosolvents led to further study of benzoyl chloride as a cosolvent<sup>23</sup> and offered some interesting and potentially promising results. However, additional studies<sup>4-6</sup> indicated that this cosolvent gave lower electrolyte conductivity and poor cathode capacity, compared with an electrolyte containing only thionyl chloride as the solvent.

Although many alternative salts have been considered, only a few were studied in detail. A gallium salt,  $\text{Ca}(\text{GaCl}_4)_2$ , was found to increase both the open-circuit potential and the average voltage on load, but capacity was only 75 percent of the  $\text{Ca}(\text{AlCl}_4)_2$  capacity.<sup>20,24</sup> The gallium salt was also found to be ineffective at retarding corrosion of calcium.<sup>23</sup>

Albeit less conductive than the calcium salt, the strontium and barium tetrachloroaluminate salts have been used by Peled to retard corrosion by altering the anode surface via exchange with the calcium in the  $\text{CaCl}_2$  passivating layer. In low concentrations, conductivity<sup>16,17</sup> of tetrachloroaluminate salts were ranked  $\text{Ca} > \text{Ba} > \text{Sr}$ . At low temperature and with high concentrations of  $\text{SO}_2$ ,  $\text{Ba}(\text{AlCl}_4)_2$  and  $\text{Sr}(\text{AlCl}_4)_2$  salts change position. The electrolyte containing the barium salt possessed the lowest viscosity; the salts of strontium and calcium were approximately equal.<sup>17</sup> Not only was corrosion in  $\text{Ba}(\text{AlCl}_4)_2$  and  $\text{Sr}(\text{AlCl}_4)_2$  electrolytes less than in  $\text{Ca}(\text{AlCl}_4)_2$ , but it was more homogeneous and free from pitting.<sup>25</sup> After storing for four weeks, 1 M solutions of Ba, Sr, and Ca tetrachloroaluminate salts showed 8, 10, and 24 percent corrosion of calcium, respectively.<sup>25</sup> The composition of the passivating layer on calcium was analyzed as follows<sup>25,26</sup>:

<u>Electrolyte Salt</u>	<u>Composition of Passivating Layer</u>
$\text{Ba}(\text{AlCl}_4)_2$	96-99% $\text{CaCl}_2$ : 1-4% $\text{BaCl}_2$
$\text{Sr}(\text{AlCl}_4)_2$	≤ 20% $\text{CaCl}_2$ : ≥ 80% $\text{SrCl}_2$



The ac spectra of  $\text{SrCl}_2$  indicated its resistivity was greater than  $\text{CaCl}_2$ , and C-size cells containing 0.7 M  $\text{Sr}(\text{AlCl}_4)_2\text{-SOCl}_2$  electrolyte did not lose capacity after four weeks storage<sup>25</sup> at 70°C. Staniewicz found that cells with  $\text{Sr}(\text{AlCl}_4)_2$  provided the same ambient temperature performance as cells with  $\text{Ca}(\text{AlCl}_4)_2$  electrolyte.<sup>20</sup>

## CATHODE STUDIES

Carbon cathode capacity in calcium cells is approximately 58 percent that of analogous lithium cells. Based on the molar volume of  $\text{CaCl}_2$ , which passivates the cathode, one would expect cathode capacity to be 80 percent that of lithium cells.<sup>3</sup> Compared to room-temperature performance of calcium cells discharged at 5 mA  $\text{cm}^{-2}$ , more than 99 percent of the cathode capacity goes unused at -30°C, but this is because severe anode polarization produces unusable load voltages.<sup>14</sup>

Cathodes are usually fabricated with Teflon binder to hold the carbon particles together. Teflon is electrically insulating, so the lower its content, the better the electrical properties of the cathode. Cathodes become too fragile to provide services below some concentration, but another way to improve their properties is to change the carbon being used. Historically, low surface area (60  $\text{m}^2 \text{g}^{-1}$ ) carbons such as Shawinigan acetylene black have been used. Carbons with higher surface areas have been used successfully to decrease current density at the cathode and to provide more numerous catalytically active reduction sites. Acetone-washed Black Pearls 2000 (BP2000, 1500  $\text{m}^2 \text{g}^{-1}$ ) gave the longest cathode life and highest load voltages in lithium surfuryl chloride cells.<sup>27</sup> Walker et al. used this approach for calcium thionyl chloride cells. Pore volume of BP2000 was 10X higher than for Shawinigan.<sup>4</sup> Acetone washing further increased pore volume, probably by removing calcium and sulfur-containing impurities introduced during the manufacturing process.<sup>4</sup> A blend of 75 percent Shawinigan (for mechanical integrity) and 25 percent acetone-washed BP2000 allowed highest operating voltage and longest capacity when compared with either Shawinigan or BP2000 alone.<sup>4-6</sup> Adding  $\text{SO}_2$  to  $\text{Ca}(\text{AlCl}_4)_2\text{-SOCl}_2$  electrolyte resulted in even further capacity improvement.

Conversely, Staniewicz found that low surface area Shawinigan, YS, and Ensagri carbons outperformed high surface area blacks.<sup>28</sup> A 1:3 blend of YS:Shawinigan gave the highest electrical capacity (24 mAh  $\text{cm}^{-2}$  at 5 mA  $\text{cm}^{-2}$ ) of carbons tested.<sup>20</sup> In his later studies,

however, a 1:3 mix of BP2000:YS with 12 percent Teflon binder was used in an optimized D-size cell.

Early studies by Higgins noted safety consequences in using high- and low-surface area cathodes.<sup>29</sup> In abuse tests, cells with high surface area cathodes burned violently and consumed the calcium. Fires in cells with low surface area cathodes were almost undetectable from normal incineration. This was explained as resulting from a 5.2 X higher surface-to-volume ratio in high surface area cells. A thick cathode with a nickel foam current collector provided a low surface area design that reduced the danger of abuse situations.<sup>30</sup>

The use of catalysts in the cathode has shown improved load voltages under high rate discharge.<sup>4-6</sup> However, at low temperatures, performance problems lie with the anode, so the added expense of catalysts would offset any marginal improvement, unless a very high rate cell were desired.

In studies by Peled et al., cell capacity was found to increase with cathode porosity from 82 to 88 percent.<sup>8</sup> However, Staniewicz et al. concluded that altering cathode porosity had little influence on performance.<sup>24,28</sup> Since the glassy  $\text{CaCl}_2$  deposit precluded full cathode utilization, it was concluded that thin, rather than thick, cathodes should be used.<sup>24,28</sup> With thinner cathodes, more cathode surface area can be fit into a cell to yield increased cell capacity. For instance, it was calculated that at  $0.024 \text{ Ah cm}^{-2}$ , a  $300 \text{ cm}^2$  "thick" cathode in a D-size cell would give 7.2 Ah, whereas a thinner and larger cathode could provide 9 Ah.<sup>20</sup>

#### ANODE AND ANODE CORROSION STUDIES

The most critical component of the calcium cell is the anode. Calcium is plagued by rapid corrosion in thionyl chloride electrolytes and by severe polarization during the low-temperature discharge, which precludes useful load voltages. A black calcium oxide film is usually present when calcium is received; but in  $\text{SOCl}_2$  solutions a new film is formed, which has been confirmed to be  $\text{CaCl}_2$  by x-ray diffraction and x-ray emission techniques.<sup>3</sup>

The kinetics of the passivating layer on calcium is described by Peled's Solid Electrolyte Interphase (SEI) model.<sup>7,31,32</sup> In essence, a metal-solution interaction forms an insoluble passivating layer that acts as a solid electrolyte; ions, not electrons, are able to

pass through the film. The LiCl SEI in lithium cells is a cationic conductor. Lithium has a transport number of about one. Therefore, during cathodic polarization (plating),  $\text{Li}^+$  is reduced at the metal/SEI interface while fresh  $\text{Li}^+$  from solution migrates through the SEI to the metal interface; the opposite occurs during cell discharge. On the other hand,  $\text{CaCl}_2$  is an anionic conductor and the transport number of  $\text{Ca}^{2+}$  is close to zero. On cathodic polarization, calcium ions are reduced at the metal/SEI interface, and anions migrate from there through the  $\text{CaCl}_2$  SEI into the solution and leave voids in the crystal lattice. Negatively charged  $\text{Cl}^-$  ions tend to accumulate because they require combination with  $\text{AlCl}_3$  to dissolve in  $\text{SOCl}_2$ . Unless there are cracks in the SEI,  $\text{Ca}^{2+}$  will not be able to migrate from solution to the calcium anode to plate out. On discharge,  $\text{Cl}^-$  ions migrate to the SEI interface and fill conducting defects to produce a more compact SEI and increase passivation. Increasing the  $\text{Ca}(\text{AlCl}_4)_2$  electrolyte concentration also increases the thickness of the passivating layer.<sup>7</sup>

Further refinements of the SEI model indicate that the SEI film is tens of angstroms thick and covered by a thicker porous passivating layer, which may reach 50 microns.<sup>16</sup> During discharge, current is carried through the SEI by  $\text{Cl}^-$  ions; although the  $\text{Ca}^{2+}$  ions that are formed need to move away from the electrode and into solution. Therefore, it is expected that the SEI cracks and reheals continually.<sup>16</sup>

It has been suggested that the open-circuit voltage (OCV) of  $\text{Ca}/\text{SOCl}_2$  is lower than theoretical calculations due to electronic leakage through the SEI whereby the corrosion current causes the voltage to drop.<sup>7</sup> It was noticed that after electrolyte is first added to a calcium cell, the OCV is <3.2 V and corrosion rates are relatively high,<sup>7,33</sup> which coincides with the dissolution of calcium oxide and building of a new  $\text{CaCl}_2$  SEI. Subsequently, the corrosion rate becomes less and cell OCV approaches 3.2 V. The impurity content of the SEI is critical for corrosion protection.<sup>34</sup>

The SEI model has been used to explain the inefficiency of plating calcium on calcium, since the SEI must be destroyed to allow  $\text{Ca}^{2+}$  to reach the metal. Peled et al. reported that a  $\text{Ca}(\text{AlCl}_4)_2$ - $\text{SOCl}_2$  cell could not be charged,<sup>35</sup> and that no practical current was observed for charging voltages up to 40 V.<sup>9</sup> Meitav reported calcium overvoltages going to 20-40 V, with the accompanying evolution of gas as thionyl chloride.<sup>7</sup> The SEI was reported to break down at about 30 V, which allowed passage of some current; however, others have re-

ported the ability to plate calcium. Cyclic voltammetric studies by Behl on passivated glassy carbon electrode in  $\text{Ca}(\text{AlCl}_4)_2\text{-SOCl}_2$  showed calcium deposition at -1.1 V versus a calcium reference.<sup>36</sup> Deposition of calcium in sulfuryl chloride was likewise seen at -1.1 V.<sup>37</sup> Also, Staniewicz et al. found that during charging the calcium overpotential of 24 V dropped to 6 V, which indicated probable cracking of the SEI to allow more efficient plating.<sup>20</sup> There is also evidence for the deposition of calcium on stainless steel. In one case, faradaic efficiency was approximately 7 percent<sup>7</sup>; in another,<sup>9</sup> a small amount of calcium was deposited at high overvoltage after prolonged electrolysis at 2 mA cm<sup>-2</sup>. There was no evidence of calcium plating on nickel electrodes.<sup>3</sup> In contrast, lithium plates onto calcium easily, with efficiency reported at 60 to 90 percent.<sup>7</sup>

One attempt to alter the SEI for better corrosion protection and/or better discharge performance was through the use of calcium alloys. Based on earlier work,<sup>38</sup> alloys with lithium were tried, which showed higher currents and load voltages than pure calcium, even though studies have shown corrosion in storage tests.<sup>23,38</sup> However, a two percent lithium alloy was later reported to reduce corrosion over pure calcium,<sup>20</sup> and by using Tafel slopes from impedance measurements, a shelf life of 5.5 years was calculated for 0.02-inch thick electrodes.<sup>34</sup> Shelf life of pure calcium and a Ca/Sb alloy were similarly calculated at 3 and 2.9 years, respectively. A calcium-antimony alloy was investigated, because it also had previously shown better current-carrying capability.<sup>39</sup> It was proposed that the beneficial effect of lithium alloys was to incorporate LiCl into the  $\text{CaCl}_2$  lattice, which would create immobile defects that pin  $\text{Cl}^-$  vacancies. This would reduce their mobility and the  $\text{Cl}^-$  diffusion rate.<sup>34</sup> Also, because LiCl is a cationic conductor, it was hoped that  $\text{Ca}^{2+}$  transport might be improved.

In addition to alloys containing Li and Sb, alloys of Ag, Sr, and Ba were also examined.<sup>10,14,20</sup> Walker concluded that there was no advantage offered over pure calcium either at room temperature or low temperature, where performance is even worse than with pure calcium.<sup>10,14</sup> A small capacity increase was seen with the Sb alloy with room temperature discharge.<sup>24</sup> Severe corrosion was noticed<sup>10,14</sup> for all alloy samples stored 60 days at room temperature in ampules containing  $\text{Ca}(\text{AlCl}_4)_2\text{-SOCl}_2$ . In comparison, lithium showed no corrosion, and it was concluded that one should use the purest calcium available.

An alternative approach to using alloys for changing the character of the SEI was by employing alternative salts. Strontium salts were found<sup>16,20,26,40</sup> to be useful in altering corrosion characteristics. Peled reported that a calcium cell with  $\text{Sr}(\text{AlCl}_4)_2\text{-SOCl}_2$  electrolyte and 7 percent  $\text{SO}_2$  stored for four weeks at 70°C showed no loss in capacity.<sup>16,26</sup> By comparison, a cell with  $\text{Ca}(\text{AlCl}_4)_2$  stored only two weeks at 70°C lost 25 to 100 percent of its capacity. After storing for four weeks, cells with the calcium salt showed 55 percent capacity loss.<sup>40</sup> In 0.4 M calcium electrolyte at 200°C, an 18 ± 3 percent weight loss was measured after 100 hours.<sup>41</sup> Other studies by Staniewicz<sup>20</sup> showed reduced corrosion after storage at 55°C for four weeks with 0.75 M Sr salt containing 20 percent V/V  $\text{SO}_2$ , compared with the Ca salt with 20 percent  $\text{SO}_2$ , which showed 50 percent capacity loss.<sup>24</sup> Analysis of the SEI<sup>26,42</sup> has shown that it is 80 percent or more  $\text{SrCl}_2$ . Without added  $\text{SO}_2$ , cells containing 1 M Sr salt have retained only 59 percent of the fresh cell capacity after comparable storage.<sup>20</sup> By increasing the  $\text{SO}_2$  concentration from 7 to 20 percent, the self-discharge rate was decreased significantly.<sup>43</sup> Other studies<sup>44</sup> with calcium foil discs have also shown reduced corrosion with the addition of  $\text{SO}_2$ .

When the barium salt was used, corrosion of calcium was reduced, although only one to four percent of the SEI<sup>26,42</sup> was composed of  $\text{BaCl}_2$ . No further work has been published about this electrolyte, and cell performance is presumed to be poor. The gallium salts,  $\text{Ca}(\text{GaCl}_4)_2$  and  $\text{Sr}(\text{GaCl}_4)_2$ , reduced corrosion, but they provided only 75 percent of the capacity realized with the tetrachloroaluminate salt.<sup>20</sup> Other salts that were studied, but which did not reduce corrosion significantly, include  $\text{Ca}(\text{SbCl}_6)_2$ ,  $\text{Ca}(\text{FeCl}_4)_2$ , (ethyl<sub>4</sub>N)  $(\text{AlCl}_4)$ ,  $\text{Li}(\text{GaCl}_4)_2$ ,  $\text{LiAlCl}_4$ , and others.<sup>3,23,29,45</sup>  $\text{LiAlCl}_4$  was found to be much less corrosive<sup>23,29,46</sup> than  $\text{Ca}(\text{AlCl}_4)_2$ , but the hazards of plating lithium would probably offset this advantage.

Walker believed that anode polarization at low temperatures was attributed primarily to mass transport properties in the electrolyte, rather than to kinetics in the SEI.<sup>10,14</sup> Polarization curves at -30°C showed that as the  $\text{Ca}(\text{AlCl}_4)_2$  concentration was increased, severe polarization occurred at lower current densities. This is in contrast to 20°C data (where mass transport is relatively high) that showed about the same polarization of calcium in 1.0 and 1.8 M solutions.<sup>10,14</sup> It was concluded that, although the SEI plays a significant role because the anode does not polarize severely at 20°C, regardless of electrolyte concentration, factors associated with decreasing temperature predominate; namely, increase in viscosity and

decrease in conductivity, mass transport, and salt solubility. Further evidence for this was obtained by following electrode OCV immediately after polarization at  $-30^{\circ}\text{C}$ . The calcium anode in 1.0 M electrolyte quickly recovered to its original potential, which suggests that the effect was mainly iR drop. However, in 1.8 M electrolyte, the calcium remained polarized on open circuit and took several minutes to achieve its original OCV. The slow return was consistent with mass-transport-related effects.

Several surface treatments have been tried, including coating calcium with cyanoacrylate. This was found to be a successful coating in lithium systems, and seemed to reduce calcium corrosion as well.<sup>20</sup> However, in a  $\text{LiAlCl}_4$  electrolyte, cyanoacrylate was found not to help storage of calcium.<sup>23</sup>

Based on work<sup>47</sup> that showed decreased anion diffusion in  $\text{SrCl}_2$  by incorporation of  $\text{Y}^{3+}$ , another suggestion (not tried) for reducing corrosion<sup>10</sup> was to substitute  $\text{Ca}^{2+}$  with  $\text{Y}^{3+}$  in the SEI. Decreased anion diffusion may in turn retard corrosion.

Formation of a synthetic SEI to overcome calcium corrosion was attempted with an rf sputtered  $\text{CaGeS}$  coating.<sup>48</sup> Coatings containing four percent  $\text{Sr}^{2+}$  or one percent  $\text{Y}^{3+}$  were also evaluated and were found to reduce corrosion; the  $\text{Y}^{3+}$  dopant appeared to enhance  $\text{Ca}^{2+}$  conduction through the SEI. Unfortunately, discharge performance in cells was worse without the coating.

## PERFORMANCE AND SAFETY

At ambient temperature, calcium cells were cathode limited, although at  $-30^{\circ}\text{C}$ , cells were limited by severe anode polarization. With increasing electrolyte concentration at low temperature, polarization became severe, even at low current densities.<sup>14</sup> At  $20^{\circ}\text{C}$ , anode polarization for 1.0 and 1.8 M  $\text{Ca}(\text{AlCl}_4)_2$  electrolyte was about the same, since mass transport is relatively high at ambient temperature.<sup>14</sup> Laboratory cell testing by Walker indicated<sup>10,14</sup> that cells with  $\text{Ca}(\text{AlCl}_4)_2\text{-SOCl}_2$  electrolyte had no usable life (load voltage above 2 V) when discharged below  $-10^{\circ}\text{C}$  at  $5 \text{ mA cm}^{-2}$ . By adding  $\text{SO}_2$  to reduce anode polarization and by using a cathode blend composed of 75 percent Shawinigan and 25 percent BP2000, a few minutes of discharge above 2 V was possible. Raising the temperature to  $-20^{\circ}\text{C}$  provided a half-hour discharge at this rate. Addition of 10 percent  $\text{Br}_2$  was also shown to improve low-temperature performance.<sup>22</sup>

Staniewicz found<sup>20,24</sup> that at  $-30^{\circ}\text{C}$ , OCV dropped to 2.55 V and load voltages above 2 V were achieved only by lowering<sup>20</sup> the load to 1.6 mA  $\text{cm}^{-2}$ . After storing for one month at  $55^{\circ}\text{C}$ , D-size cells had no usable capacity above 2.5 V at ambient temperature when discharged at a 2 A rate.<sup>49</sup> Capacity was 3.6 Ah to zero volts, a loss in capacity of more than 50 percent. It is apparent that use of  $\text{Ca}(\text{AlCl}_4)_2\text{-SOCl}_2$  electrolyte will not permit a viable system.

Staniewicz et al. tested an optimized  $\text{Ca/SOCl}_2$  system consisting of a calcium anode, 25/75 weight blend of BP2000 and YS carbon, and 0.75 M  $\text{Sr}(\text{AlCl}_4)_2\text{-SOCl}_2$  with 20 percent V/V  $\text{SO}_2$ . Fresh D-size cells discharged at 2 A constant current provided 8.9 Ah (19 mAh  $\text{cm}^{-2}$  cathode area) at ambient temperature<sup>20</sup> and 5.3 Ah (11 mAh  $\text{cm}^{-2}$ ) at  $-30^{\circ}\text{C}$ . Wade et al.<sup>50</sup> stored some of these cells either at room temperature or  $55^{\circ}\text{C}$  and then discharged them at low rate (1, 2, or 4 mA  $\text{cm}^{-2}$ ) under ambient and  $-30^{\circ}\text{C}$  conditions. Results (listed here) indicate significant corrosion of calcium had occurred, since poor capacities, even under low drains, were observed at both ambient and  $-30^{\circ}\text{C}$ .

Storage	RT Capacity/ Ah	$-30^{\circ}\text{C}$ Capacity/ Ah	Comments
1 month RT	5.6	3.35	---
4 month RT	0 to 5	0.6 to 3	some vented
2 month RT & 1 mo $55^{\circ}\text{C}$	1.1	not done	low OCVs (only 1 of 7 cells gave meaningful data)

The conclusion was that this chemistry has a shelf life of less than 10 months,<sup>50</sup> which is in contrast to a report by Peled et al., which projected<sup>26</sup> an expected shelf life of longer than three years at  $20^{\circ}\text{C}$  with the Sr electrolyte + 7%  $\text{SO}_2$ . He responded to this data by claiming that the use of nickel plated steel cans (used by Staniewicz) promoted corrosion, and only pure stainless steel should be used. As part of a European Research Office contract, Peled delivered C-size cells for evaluation to the same group in the spring of

1990. The cells containing 0.84 M  $\text{Sr}(\text{AlCl}_4)_2$  and 20 percent  $\text{SO}_2$  were discharged at a 0.7 A (approximately  $3.2 \text{ mA cm}^{-2}$ ) rate at ambient temperature, as recommended by Peled. Capacity to a 2.0 V cutoff averaged 3.85 Ah for two fresh cells (4.0, 3.7 Ah). After storing for one-month at  $55^\circ$ , the average capacity was 3.3 Ah on a four-cell sample (4.0, 3.7, 3.5, 2.0 Ah). Two fresh cells that were discharged at a 0.1 A rate at  $-30^\circ\text{C}$  gave no capacity to a 2.0 V cutoff. Note that, in addition to the can material, there were several other differences between Staniewicz's and Peled's cells, which may also account for discrepancies in performance; specifically, the calcium stock and purity, selection of carbon in the cathode, electrolyte concentration, and moisture content of cell assembly areas. Although there was some variation in Peled's data, indications are that it is possible to carefully engineer this cell chemistry to reduce corrosion significantly.

Microcalorimetric studies by Peled on  $\text{Ca}(\text{AlCl}_4)_2\text{-SOCl}_2$  C-size cells showed heat output of  $450 \mu\text{W}$  one week after cell assembly.<sup>51</sup> A modified cell of undisclosed chemistry, but which presumably contained the Sr electrolyte, showed lower heat output.<sup>51</sup> In cells containing the Sr electrolyte, discharge capacities after one month storage at  $71^\circ\text{C}$  were similar (only 6 percent loss) to those of fresh cells.<sup>16,26,40</sup> However, at  $-30^\circ\text{C}$ , cells with the Sr electrolyte provided less capacity than the  $\text{Ca}(\text{AlCl}_4)_2$ -containing cells.<sup>16,40</sup> Increasing electrolyte concentration and adding  $\text{SO}_2$  increased the capacity at  $-30^\circ\text{C}$ , but it still fell short of that obtained with the calcium salt.

In earlier safety tests, fires were reported<sup>29,30</sup> from incineration and penetration by bullets, but a thick cathode with a nickel foam current collector reduced the danger. No condition produced a hazardous response in these cells in sizes as large as 600 Ah.<sup>30</sup>

Generally, in more recent studies with either the Ca or Sr electrolyte, the most serious result from abuse tests has been cell venting. This is an improvement over lithium cells, yet it suggests that development of a ventless cell may not be feasible without a thicker can or additional safety improvements. The use of a Tefzel separator can provide added safety on short circuit.<sup>16</sup> As temperature goes up, the Tefzel will melt and the pores will close, which will increase cell resistance effectively and act as an internal fuse.



## CONCLUSIONS

The premise that the Ca/SOCl<sub>2</sub> system is safer than Li/SOCl<sub>2</sub> has been substantiated. The worst-case scenario from abuse appears to be cell ventings.

Although cathode capacities are less than expected during ambient temperature discharge, they are reasonably good. Best performance is achieved when using a cathode composed of a blend of high- and low-surface area carbons in combination with SO<sub>2</sub> added to the electrolyte.

A persistent performance problem lies with the anode during low-temperature discharge. The reasons for severe polarization are attributable to the CaCl<sub>2</sub> SEI and the decreased mass transport. Attempts to modify the SEI to enhance protection from corrosion by use of calcium alloys were unsuccessful. Modification through the use of Sr(AlCl<sub>4</sub>)<sub>2</sub>-SOCl<sub>2</sub> electrolyte has reduced corrosion, but has also diminished low-temperature performance. The addition of SO<sub>2</sub> improved electrolyte conductivity and enhanced mass transport to decrease anode polarization under load. Raman and NMR studies have shown that SO<sub>2</sub> acts to solvate Ca<sup>2+</sup>, similar to that observed for Li<sup>+</sup> in LiAlCl<sub>4</sub>-SOCl<sub>2</sub> solutions.<sup>52</sup> The addition of Br<sub>2</sub> also improved low-temperature anode performance. However, although slight improvements have been made, no one has been able to demonstrate reasonable low-temperature performance. It is expected that battery packs that are discharged at low temperatures should produce enough waste heat to increase cell temperature and thereby increase capacity and load voltage.<sup>10,14,20</sup>

The most useful cell chemistry seems to be one which contains a pure calcium anode combined with a Sr(AlCl<sub>4</sub>)<sub>2</sub> electrolyte containing 20 percent added SO<sub>2</sub> for improved corrosion protection and performance. A thin cathode of blended high- and low-surface area carbons seems to offer best cathode performance.

Commercial development of a calcium-thionyl chloride battery has been impeded by the shortfalls discussed, and enthusiasm for this system has dwindled. Considering its safety features, if a ventless cell can be designed, it may have use in special applications such as closed environments. This chemistry may also be useful in high-temperature environments (where lithium is molten) or in reserve cell applications. However, use at low temperatures does not appear

and electrolyte chemistry. Although interest is limited, work on this chemistry continues, primarily by Peled and coworkers.

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